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# Limitations to the quantitative application of Cd as a paleoceanographic tracer, based on results of a multi-box model (MENU) and statistical considerations

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## ABSTRACT

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The distribution of cadmium in the modern ocean gives important information about ocean circulation and nutrient distributions. As the Cd/Ca-ratio of foraminiferal shells is proportional to that of seawater, Cd/Ca-records of benthic foraminifera have been used to reconstruct the Glacial oceanic distributions of dissolved Cd and PO<sub>4</sub> quantitatively. The results, in turn, have served as boundary conditions for ocean carbon cycle models. This quantitative reconstruction, however, requires that the present oceanic Cd–PO<sub>4</sub> relationship and the distribution coefficient converting Cd/Ca-ratios into dissolved Cd and PO<sub>4</sub> concentrations, remain constant through geological time.

We have constructed a multi-box model (MENU: metal-nutrients) to test various hypotheses about the biogeochemical mechanisms determining the modern oceanic Cd–PO<sub>4</sub> relationship and its behaviour in time. The results indicate that the oceanic Cd–PO<sub>4</sub> relationship may change in response to changing oceanic conditions, such as circulation, productivity changes and upwelling intensity, for example during a glacial period. In addition, we discuss the frequent omission in the literature of statistical considerations pertaining to regression analysis, resulting in an unduly optimistic estimate of the distribution coefficient, thereby neglecting uncertainties on the order of 30% or more. In combination with spatial variability of the distribution coefficient, this conceivably poses intrinsic restrictions to its use as a conversion factor.

We conclude that, awaiting a significant reduction of the aforementioned uncertainties, interpretation of the sedimentary Cd/Ca record should be performed only qualitatively.

## Introduction

Ocean circulation and oceanic nutrient distributions (more specifically phosphate, PO<sub>4</sub> and nitrate, NO<sub>3</sub>) are important variables in scenarios trying to explain the 80 ppmv shift in atmospheric CO<sub>2</sub> content between Glacial and Interglacial times (Broecker and Peng, 1986; Broecker and Peng, 1987; Boyle, 1988c; Boyle, 1988b; Sarmiento et al., 1988b; Volk and Liu, 1988; Keir, 1989; Keir, 1990; Peng and Broecker, 1991). Hence, they are also important variables in models forecasting the possible climatic effects of the increase in atmospheric CO<sub>2</sub> content due to an-

thropogenic emissions. In addition, since biological productivity in large parts of the world oceans is limited by low surface water concentrations of PO<sub>4</sub> and NO<sub>3</sub>, the availability of which is to a large extent determined by the rate of upwelling of abyssal waters, knowledge of paleonutrient distributions and paleocirculation is of importance also in studying paleoproductivity (Bishop, 1989; Keir, 1989; Martin, 1990).

The oceanic distributions of PO<sub>4</sub> and NO<sub>3</sub> are controlled by a combination of their involvement in the biological cycle and the oceanic thermohaline circulation (Broecker and Peng, 1982). Nutrients could thus, in principle, serve as tracers for

both paleonutrient distributions and paleocirculation. However, since the oceanic distributions of these nutrients are not directly preserved in the sedimentary record, other, indirect tracers must be used. Both cadmium (Cd) and carbon-13 ( $^{13}\text{C}$ ) have seawater distributions very similar to those of  $\text{PO}_4$  and  $\text{NO}_3$  (Boyle et al., 1976; Bruland et al., 1978; Bruland, 1980; Kroopnick, 1985) and of both elements their dissolved distributions are recorded in foraminiferal shells (Boyle, 1986; Boyle, 1988a; Boyle, 1992). The paleoceanographic applications and limitations of  $^{13}\text{C}$  have been extensively discussed in the literature (Shackleton, 1977; Boyle and Keigwin, 1982; Shackleton et al., 1983; Duplessy et al., 1984; Boyle, 1986; Boyle and Keigwin, 1987; Curry et al., 1988; Broecker, 1992) and will not be addressed. Here, we want to focus on the restrictions to a *quantitative* interpretation of the sedimentary Cd/Ca-record.

The modern oceanic distributions of dissolved Cd,  $\text{PO}_4$  and  $\text{NO}_3$  are closely correlated (Boyle et al., 1976; Bruland et al., 1978; Bruland, 1980). At individual stations, property-property plots of Cd versus  $\text{PO}_4$  (or  $\text{NO}_3$ ) often approximate a linear correlation which is highly significant statistically ( $r \geq 0.9$ ;  $\alpha < 0.01$ ). Hereafter,  $\text{PO}_4$  will be used as the reference nutrient, but the discussion is generally valid for  $\text{NO}_3$  as well. From a compilation of eight Atlantic and north Pacific data sets for waters below the mixed layer, it was concluded that the relationship between Cd and  $\text{PO}_4$  was uniform globally (Boyle, 1988a; Table 1). This uniformity has recently been questioned and the oceanic Cd- $\text{PO}_4$  relationship has been revisited (De Baar et al., submitted; Table 1).

TABLE 1

Coefficients of linear regression of Cd on  $\text{PO}_4$ 

Reference	Seawater relationship: $\text{Cd (nM)} = a \times \text{PO}_4 (\mu\text{M}) + b$		
	a	b	
Boyle, 1988	0.2	0	( $\text{PO}_4 < 1.3 \mu\text{M}$ )
	0.4	-0.25	( $\text{PO}_4 > 1.3 \mu\text{M}$ )
De Baar et al. (submitted)	0.15	0.065	( $\text{PO}_4 < 2.0 \mu\text{M}$ )
	0.38	-0.15	( $\text{PO}_4 > 2.0 \mu\text{M}$ )

TABLE 2

Distribution coefficient,  $D = \text{Cd}/\text{Ca}_{\text{foram}} : \text{Cd}/\text{Ca}_{\text{seawater}}$ 

Reference	D	Error
Delaney, 1989	2-4	33%
Boyle, 1988	2.6	> 0.6 linear regression
	2.9	$\pm 0.6$ based on histogram

In the early eighties, Boyle and coworkers (Boyle, 1981; Hester and Boyle, 1982; Delaney, 1989) demonstrated that Cd appeared to be incorporated into foraminiferal shells in proportion to its ambient seawater concentration. The "distribution coefficient" ( $D$ ), relating the Cd/Ca ratio of the foraminiferal shell to that in seawater, was assessed in two ways. Using a radioactive Cd-tracer in culture studies of *planktonic* foraminifera,  $D$  was determined directly (Delaney, 1989; Table 2). An indirect estimate of  $D$  was determined by comparing Cd/Ca ratios in various *benthic* foraminiferal species obtained from box-core tops, with the ambient bottom water  $\text{PO}_4$  concentration (obtained from the GEOSECS expeditions) (Hester and Boyle, 1982; Boyle, 1988a). Relying on the relationships in Table 1,  $D$  was calculated for each box-core top and for each species (Table 2). In order to guarantee that bioturbation did not introduce Glacial foraminifera into Holocene sediments, only those box-cores were selected where isotopic stratigraphy indicated more than 15 cm of Holocene sediment (hereafter called documented cores) (Boyle, 1988a; Boyle, 1992). With the above relations for  $D$  and Cd- $\text{PO}_4$  (Tables 1 and 2), the Cd/Ca record of benthic foraminifera has been used for a quantitative reconstruction of the paleoceanographic distributions of dissolved Cd or  $\text{PO}_4$ , which, in turn, have been interpreted in terms of paleonutrient distributions and/or paleocirculation (Boyle, 1986; Boyle and Keigwin, 1987; Curry et al., 1988; Duplessy et al., 1988; Broecker and Denton, 1989; Boyle, 1990; Delaney, 1990). These paleoceanographic reconstructions have served as boundary conditions for numerical simulations, modelling paleoproductivity and the 80 ppmv shift in atmospheric  $\text{CO}_2$  content between the last Glacial and the Holocene, see above.

In order to interpret the Cd/Ca-record quantitatively, two conditions have to be met:

(1) The modern oceanic Cd-PO<sub>4</sub>-relationship must be constant in time.

(2) The distribution coefficient,  $D$ , must be calibrated independently and there must be no reason to suspect its changing in time.

Mostly, it is common (and good) practice to assume constancy in time of present-day relationships in absence of compelling arguments to the contrary. However, in this paper we argue that, thus far, neither of the above two conditions seems to hold for the geological past.

We discuss the results of a numerical simulation model (MENU), which was developed to test various hypotheses about the biogeochemical mechanisms determining the oceanic distributions of Cd and PO<sub>4</sub> and to evaluate the influence of changing oceanic conditions between Glacial and Interglacial times on the seawater Cd-PO<sub>4</sub> relationship. Prior to the model the modern Cd-PO<sub>4</sub> relationship is reviewed briefly. After the model we shall deal with statistical considerations pertaining to quantitatively estimating Cd, PO<sub>4</sub> or  $D$  from property-property plots. Lastly, the problems associated with an accurate determination of  $D$  will be discussed.

## Results

### *The relationship between Cd and PO<sub>4</sub> in modern seawater*

#### *Trends*

A recent, complete review of the presently available Cd dataset will form the basis of the following discussion (De Baar et al., submitted). In that paper a selection criterion was applied to ensure the inclusion of exclusively high-precision Cd and PO<sub>4</sub> data. The selection criterion does not guarantee high accuracy of the datasets.

The traditional approach of studying metal-nutrient relationships is from property-property plots of the entire watercolumn (sometimes with exclusion of surface waters, e.g. Boyle et al., 1976; Bruland, 1980; Boyle, 1988a; Westerlund and Öhman, 1991; Frew and Hunter, 1992). However, the main reason such analyses must be viewed

with caution is that several water masses are intersected, each with completely different biogeochemical and physical characteristics. In open ocean surface waters, concentrations of metals and nutrients are largely determined by a balance between upwelling and removal by primary producers. In the permanent thermocline, remineralization of organic material and mixing are important processes and in abyssal waters mixing between water masses plays a dominant role. Plotting these data into one graph furthermore obscures regional trends due mainly to the fact that most of the spread of the data is caused by thermocline waters (Figs. 4 and 5), spanning a concentration range from low (sub)surface water values to maximum values at the base of the thermocline. Important water masses each with different preformed Cd and PO<sub>4</sub> concentrations and Cd/PO<sub>4</sub> ratios, are for example the North Atlantic Deep Water-complex (NADW), Antarctic Bottom Water (AABW) and Antarctic Intermediate Water (AAIW).

Ideally, one would like to follow the chemical evolution of a well-defined water-type at specific density surfaces. However, this approach calls for an accurate study of the hydrography of waters and most trace metal papers are scant on hydrography. A compromise would be to at least separate surface waters, permanent thermocline waters and thermohaline driven deep waters (deeper than  $\approx 1000$  m) and study property-property plots for each of these water-types. Labelling of samples would enable the analysis of regional trends.

A more instructive picture is obtained from plotting the Cd/PO<sub>4</sub> ratio as a function of water-depth (Fig. 1). In case of ideal, functional covariation between both elements, the ratio should remain constant vertically over large areas (Fanning, 1992). However, since precision and accuracy of the data strongly decrease with low concentrations, the ratio exhibits large error near the surface. This is shown schematically in Fig. 2. For almost all datasets, Cd and PO<sub>4</sub> do not show ideal covariation (Fig. 1). Cd/PO<sub>4</sub> ratios are low in surface waters (50–200 pmol/ $\mu$ mol). Lowest values are observed for oligotrophic gyres (30–100 pmol/ $\mu$ mol cf. Bruland, 1980), whereas up-

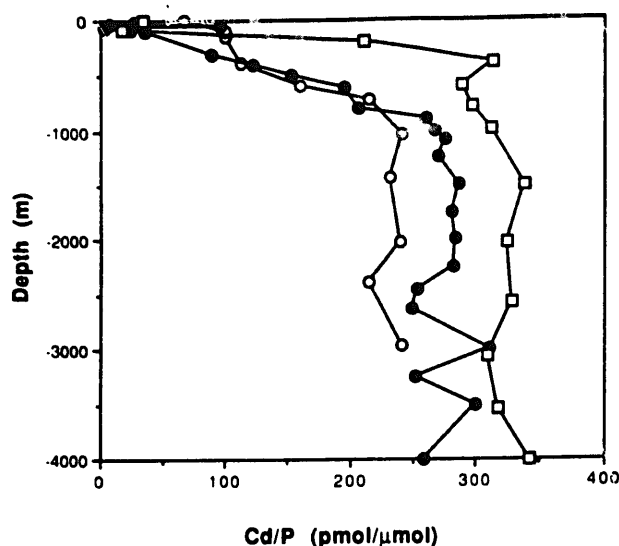


Fig. 1. Vertical profiles of Cd/PO<sub>4</sub> ratio (pmol/μmol). Data are from northwest Atlantic Ocean, open circles (Bruland and Franks, 1983), west equatorial Indian Ocean, closed circles (Morley et al., in press) and northeast Pacific Ocean, open squares (Bruland, 1980).

welling areas have high ratios (100–200 pmol/μmol, cf. Saager et al., 1992). Cd/PO<sub>4</sub> ratios strongly increase in the upper thermocline, reach a maximum at or above the individual dissolved maxima of Cd and PO<sub>4</sub> and remain constant below this depth. As we shall see below, latter feature is important in discriminating between

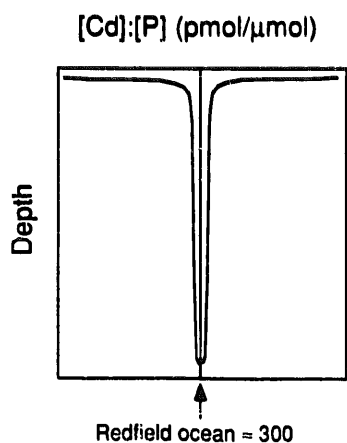


Fig. 2. Theoretical profile of Cd/PO<sub>4</sub> ratio (pmol/μmol) for a Redfield Ocean where no fractionation between Cd and PO<sub>4</sub> occurs. The error envelope, given by its width,  $W$  is a function of the coefficients of variation (C.V.) of the Cd and PO<sub>4</sub> measurements:  $W = 4 \times (Cd/PO_4) \times \{(C.V._{Cd})^2 + (C.V._{PO_4})^2\}^{0.5}$ , note the rapid increase in  $W$  in the upper watercolumn due to increasing errors on the Cd and PO<sub>4</sub> measurements at low concentrations.

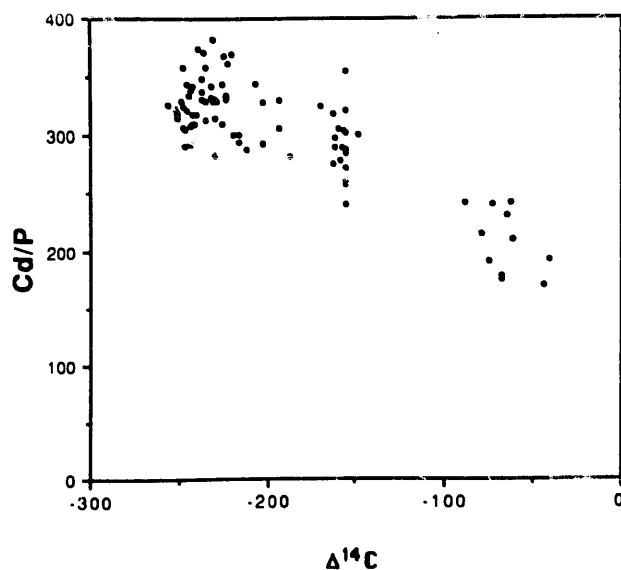


Fig. 3. Cd/PO<sub>4</sub> ratio (pmol/μmol) of thermohaline driven deep waters, versus  $\Delta^{14}C$  values (‰). Only high quality Cd data were used. Carbon-14 values were estimated from the nearest GEOSECS stations (Östlund and Stuiver, 1980; Stuiver and Östlund, 1980; Stuiver and Östlund, 1983) at corresponding density or, in absence of information on hydrography, at corresponding depth intervals. Care was taken to ensure characterization of correct water masses. Vertical variability of  $\Delta^{14}C$  in deep waters remains constant over large areas. The error in the  $\Delta^{14}C$  values is probably not larger than  $\pm 10$ – $15$ ‰. However, since stations do not match in time and space, the data must be regarded as a trend only.

two mechanisms which may account for this pattern. In the thermohaline driven deep waters, the Cd/PO<sub>4</sub> ratio increases with the age of the water (Figs. 1, 3 and 4). A step-wise increase of the Cd/PO<sub>4</sub> ratio from 200 pM/μM to 280 pM/μM occurs at the transition from NADW to AABW (Figs. 3 and 4). After the Antarctic, the deep ocean circulation is dominated by Antarctic and recirculated Antarctic waters (Broecker et al., 1985) and Cd/PO<sub>4</sub> ratios in deep waters gradually increase from the Antarctic (280 pmol/μmol) to the northeast Pacific Ocean (330–350 pmol/kg).

The lack of ideal covariation is further reflected by the significant non-zero intercepts in the deep water property–property plot of Cd versus PO<sub>4</sub> (Fig. 4). Clearly, two different deep water provinces can be distinguished, exhibiting statistically significantly different Cd–PO<sub>4</sub> relationships. A property–property plot of the ther-

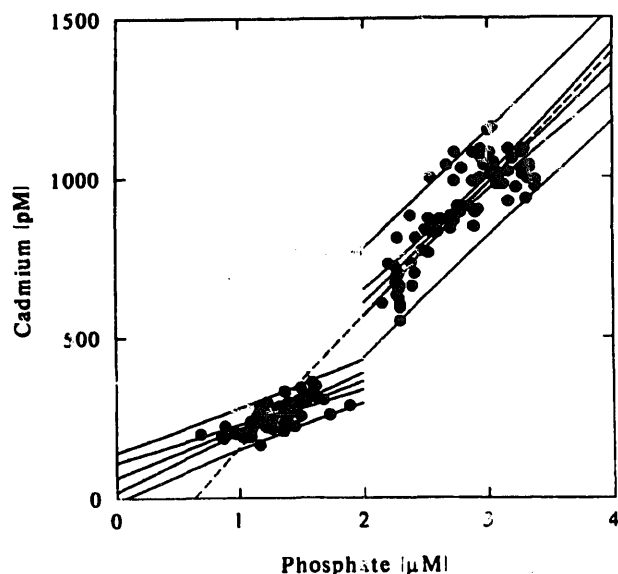


Fig. 4. Property-property plot of Cd (pmol/kg) versus  $\text{PO}_4$  ( $\mu\text{mol/kg}$ ) for thermohaline driven deep waters (high quality data only), redrawn after De Baar et al., submitted. The distribution is significantly bimodal, hence two relations must be used, one for  $\text{PO}_4 > 2.0 \mu\text{mol/kg}$ , one for  $\text{PO}_4 < 2.0 \mu\text{mol/kg}$ . In the plot regression lines obtained by ordinary least squares regression (OLS) are drawn with corresponding 95% confidence intervals on the slope  $b$  and the entire population (the latter must be used for predicting Cd at given  $\text{PO}_4$ ). The dashed line is the regression on the entire population, when ignoring the bimodality.

mocline region only (Fig. 5), also shows different Cd/ $\text{PO}_4$  slopes for the north Atlantic ( $\approx 200 \text{ pmol}/\mu\text{mol}$ ) and the other oceans ( $300\text{--}350 \text{ pmol}/\mu\text{mol}$ ; no data has as yet been published for the South Atlantic Ocean). Thermocline waters have small non-zero intercepts for Cd versus  $\text{PO}_4$ , as they bridge surface waters with virtually zero Cd and  $\text{PO}_4$  concentrations and deep waters with high concentrations. Note that, although Indo-Pacific deep waters and thermocline waters have largely similar Cd/ $\text{PO}_4$  ratios, deep water slopes are higher ( $400 \times 10^{-6}$  versus  $330 \times 10^{-6}$ ) due to the large non-zero intercept.

#### Mechanisms

The trends of the Cd- $\text{PO}_4$  relationship are compatible with the following processes. In surface waters Cd and  $\text{PO}_4$  are fractionated. Theoretically, two fractionation processes can be envisioned (Boyle et al., 1981; Collier and Edmond, 1984). Cd is preferentially incorporated by pri-

mary producers and/or  $\text{PO}_4$  is preferentially excreted by grazers. Both processes lead to low Cd/ $\text{PO}_4$  ratios in surface waters and high ratios in sinking organic matter. Subtle trends have been observed in surface waters enabling a tentative discrimination between both fractionation processes, but these do not affect the present discussion. However, preferential remineralization of  $\text{PO}_4$  should be largely restricted to grazers producing  $\text{PO}_4$  depleted fecal pellets, and cannot be persistent throughout the entire watercolumn. For, in that case the dissolved maxima of Cd and  $\text{PO}_4$  would be decoupled vertically, as is the case with for example  $\text{PO}_4$  and Si. The latter element has a significantly deeper remineralization cycle than  $\text{PO}_4$  (Broecker and Peng, 1982). A statistically significant decoupling of the dissolved maxima of Cd and  $\text{PO}_4$  (and consequently increasing Cd/ $\text{PO}_4$  ratios with depth below the thermocline, other than due to transitions between different water masses), has been observed in only very few published datasets (De Baar et al., submitted). Some fractionation during remineralization cannot be precluded in view of the precision of the data and the resulting Cd/ $\text{PO}_4$  ratios.

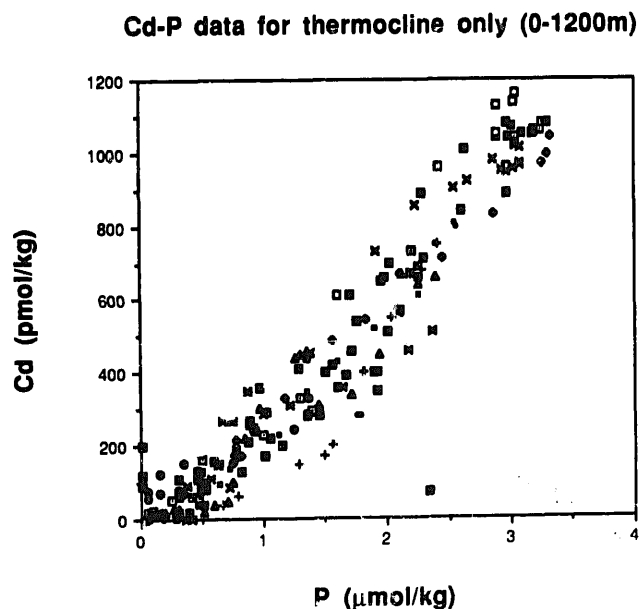


Fig. 5. Property-property plot of Cd (pmol/kg) versus  $\text{PO}_4$  ( $\mu\text{mol/kg}$ ) for thermocline waters,  $\approx 0\text{--}1200 \text{ m}$  depth (high quality data only, references given in De Baar et al., submitted). Note the significantly smaller intercepts than for deep waters.

In the thermocline, remineralization of dissolved or sinking particulate organic matter (POM) releases both elements into solution. As the organic matter has high  $\text{Cd}/\text{PO}_4$  ratios, the dissolved ratio increases with depth. In addition, horizontal and vertical mixing with deep water masses ultimately determines the observed vertical gradients of dissolved Cd,  $\text{PO}_4$  and the  $\text{Cd}/\text{PO}_4$  ratio. The difference in  $\text{Cd}/\text{PO}_4$  slope between thermocline waters of the Atlantic and the Indo-Pacific Oceans may be due to a difference in composition of organic matter, but may also be due to mixing between thermocline waters and North Atlantic Deep Water with low  $\text{Cd}/\text{PO}_4$  ratios in the north Atlantic Ocean, and mixing between thermocline waters and Antarctic water masses with high  $\text{Cd}/\text{PO}_4$  ratios in the other oceans. Consequently, the thermocline slope does not solely reflect the regenerative ratio of Cd versus  $\text{PO}_4$ .

The step-wise increase of the deep water  $\text{Cd}/\text{PO}_4$ -ratio mentioned above may be crucial to the behaviour of the Cd- $\text{PO}_4$  relationship in time. It probably derives from the fact that at the formation areas of NADW and AABW, deep waters are created with a preformed  $\text{Cd}/\text{PO}_4$ -signal. The preformed  $\text{Cd}/\text{PO}_4$  ratio of NADW is substantially lower than that of AABW. The fact that  $\text{Cd}/\text{PO}_4$  ratios increase with the age of the deep water (Fig. 3) is due to the continuous remineralization of organic matter with high  $\text{Cd}/\text{PO}_4$  ratios. It has also been suggested that this kink in the Cd- $\text{PO}_4$  plot would be caused by the intrusion of AAIW, carrying low preformed  $\text{Cd}/\text{PO}_4$  ratios (Doroshevich and Boyic, 1992; Frew and Hunter, 1992). However, no data are available from waters positively identified as AAIW source waters (Antarctic Convergence). Samples taken in the vertical watercolumn, intersecting the AAI-water mass have  $\text{Cd}/\text{PO}_4$  ratios similar to those in AABW (260–300  $\text{pmol}/\mu\text{mol}$ ) (Statham, 1983; Yeats, pers. comm., 1992; Frew and Hunter, 1992). Hence, the low ratios of NADW are sandwiched between high ratios of AAIW and AABW. Because deep Atlantic water has a relatively short residence time, its low  $\text{Cd}/\text{PO}_4$  ratio may reflect the relatively small contribution of regenerative input relative to pre-

formed concentrations. It is thus to be expected that in case of a longer residence time of Atlantic deep waters, the regenerative contribution will increase and the  $\text{Cd}/\text{PO}_4$  ratio will change.

Summarizing, the  $\text{Cd}/\text{PO}_4$  ratio is variable in *three* dimensions. The distribution of the  $\text{Cd}/\text{PO}_4$  ratio in the oceans is controlled by a fractionation process in surface waters, transmitted to deep waters by the biological pump. The oceanic deep water circulation creates an asymmetry between the oceans not only in deep water Cd and  $\text{PO}_4$  concentrations, but also in  $\text{Cd}/\text{PO}_4$  ratios. We shall now consider the question whether the present relationship is likely to remain constant through geological time, in order to allow a reconstruction of paleo-nutrient distributions.

### Modelling Cd and $\text{PO}_4$ in the Interglacial and Glacial oceans

Although the present-day relationship between Cd and  $\text{PO}_4$  is not constant in space, what we really want to know is whether it should be expected to be constant in time. Four factors presumably determine the relationship between Cd and  $\text{PO}_4$ :

- (1) thermohaline circulation;
- (2) the  $\text{Cd}/\text{PO}_4$ -ratio of remineralizing organic material as determined by fractionation processes in surface waters
- (3) the contribution of preformed deep water concentrations of Cd and  $\text{PO}_4$  and their  $\text{Cd}/\text{PO}_4$  ratios
- (4) the oceanic Cd and  $\text{PO}_4$  inventories.

Let us consider a few often used scenarios for the Glacial ocean. These include a significant reduction, though no cessation, of North Atlantic Deep Water formation (Boyle and Keigwin, 1985/1986), an increased productivity in upwelling areas of oceanic boundaries due to increased wind stress fields and a change in Antarctic productivity. Besides scenarios calling for increased Antarctic productivity, it is interesting to note that there appears to be evidence for lower productivity during Glacial times (Mortlock et al., 1991), so that this region is in fact open to a wide range of scenarios.

If NADW formation would be reduced, the assymetry between the oceans would be partly alleviated. The reduced assymetry between the oceans is supported by the downcore Cd/Ca and  $^{13}\text{C}$  records from the Atlantic and Pacific Oceans (Boyle, 1992). This would imply a longer residence time of Atlantic deep waters and a reduced contribution of the northern deep water component with its low preformed Cd and  $\text{PO}_4$  concentrations and low Cd/ $\text{PO}_4$  ratio. As a result, the oceanic deep water Cd/ $\text{PO}_4$  ratios may converge to an intermediate value for the Atlantic and Indo-Pacific oceans. If primary productivity in the Antarctic Ocean substantially increases, its preformed Cd and  $\text{PO}_4$  concentrations decrease, and probably so does its preformed Cd/ $\text{PO}_4$  ratio due to fractionation in surface waters. In that case the non-zero intercept of the deep water Cd- $\text{PO}_4$  plot may shift towards the origin. In absence of a significant preformed signal, the deep water *ratio* would then become dominated by the regenerative input-ratio ( $\approx 400 \text{ pmol}/\mu\text{mol}$  for the modern ocean). If Antarctic productivity decreases during Glacial times, the effects probably will be less dramatic, since today Antarctic surface waters already carry a significant preformed signature as a result of incomplete consumption of nutrients.

It has been suggested that surface organic material has fairly constant Cd/ $\text{PO}_4$  ratios in spite of a large range in dissolved concentrations and ratios (Collier and Edmond, 1984). However, suspended particulate matter fully dominated by diatoms, has significantly lower Cd/ $\text{PO}_4$  ratios than in case of the presence of other primary producer taxa (Collier and Edmond, 1984; Noriki et al., 1985). This implies that in case of a shift in the ratio of diatom producers to non-diatom producers between Glacial and Interglacial times, the regenerative ratio of organic material may be different from that of today. There is evidence that the atmospheric dust load during Glacial times was much higher than during Interglacial times (Royer et al., 1983). More dust would imply an increased input of Fe into surface waters (Martin, 1990). Studies on the influence of Fe on phytoplankton suggest that large diatoms may be stimulated by high Fe concentrations (Hudson and Morel, 1990; Buma et al., 1991; Price et al., 1991). As diatoms flourish in polar regions (Johnson, 1957), this may yield the Antarctic productivity scenario for a Glacial period rather unpredictable.

There seem to be plenty of reasons to expect a significant change in the Cd- $\text{PO}_4$  relationship between Glacial and Interglacial times. In order

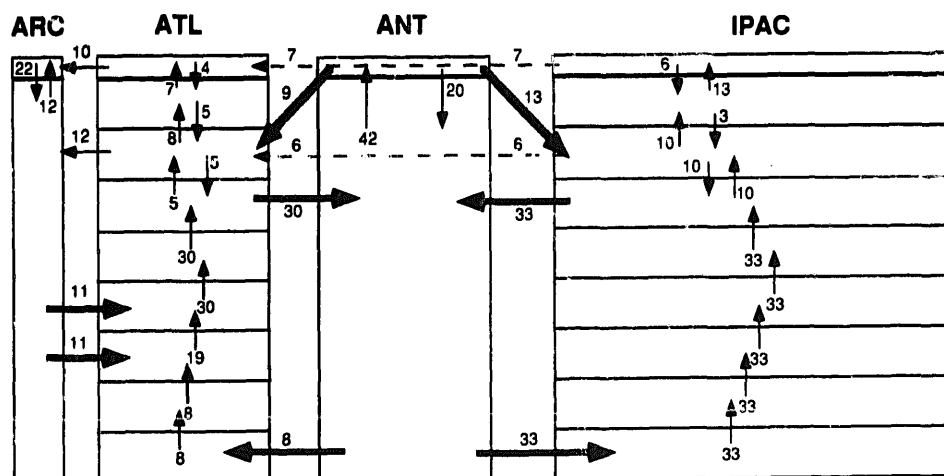


Fig. 6. Configuration of MENU. Scheme of advective water fluxes is adapted after CYCLOPS (Keir, 1988) and PANDORA (Broecker and Peng, 1986) models. ARC = northern North Atlantic, ATL = temperate Atlantic Ocean, ANT = Southern or Antarctic Ocean, IPAC = Indo-Pacific Ocean. All fluxes are in sverdrups ( $10^6 \text{ m}^3 \text{ s}^{-1}$ ). Other model parameters are given in Table 3. Bold arrows correspond to major water masses, North Atlantic Deep Water, Antarctic Bottom Water, Antarctic Intermediate Water, Common Water. Surface layer is 100 m thick, other layers are 450 m each for Atlantic and Indo-Pacific boxes, 3600 m for polar boxes.



to test some of the aforemade assumptions about the processes influencing the Interglacial and Glacial Cd-PO<sub>4</sub> relationship, we developed a multi-box model, MENU, to simulate the oceanic distributions of trace metals and nutrients.

#### *The model MENU (metal-nutrients)*

The purpose of MENU is to evaluate various hypotheses about processes controlling the oceanic distributions of Cd and PO<sub>4</sub> during Interglacial and Glacial times. Like most box-models, an accurate simulation of the actual distributions of Cd and PO<sub>4</sub> cannot be aimed at. Important reasons for this are first that within reasonable limits, the configuration of the model (Fig. 6) has been kept as simple as possible, while still yielding enough spatial information. Also, apart from qualitative information about the involvement of Cd in the biological cycle derived from its dissolved distribution, little quantitative information is available about its uptake by phytoplankton, excretion by grazers, particulate distribution, remineralization from organic material and so on (Collier and Edmond, 1984; Noriki et al., 1985; Abe and Matsunaga, 1988; Sherrell, 1989; Price and Morel, 1990; Sherrell and Boyle, 1992). For this reason, a more elaborate model cannot be well constrained. By comparing "Glacial type" conditions with Interglacial conditions we only try to test the hypothesis whether or not it is reasonable to assume the modern Cd/PO<sub>4</sub>-relationship to remain constant in time. The results should not be considered as an attempt to reconstruct the most likely relationship for a Glacial period. The model is explanatory, not predictive. Differential equations in MENU are not solved, but integrated numerically with Euler's rectangular method using time steps small in comparison with the smallest time constants (primary productivity).

#### *Model configuration*

The configuration of MENU is depicted in Fig. 6 together with its thermohaline circulation pattern. We have divided the ocean into two polar regions and two low latitude regions, one for the Atlantic Ocean and one for the combined Indo-Pacific Ocean. In this way no excessive detail is introduced, while the asymmetry in the oceanic

distributions of metals and nutrients could still be simulated. We have opted for a significant amount of vertical resolution in the temperate oceans in order to gain more detailed information about the vertical distributions of Cd, PO<sub>4</sub> and the Cd/PO<sub>4</sub> ratio than could be obtained from previous box-models (CYCLOPS: Keir, 1988; PANDORA: Broecker and Peng, 1986). In the polar regions only two layers were distinguished. These are areas of deep water formation and physical parameters indicate a well-mixed, homogenous watercolumn with little vertical stratification (Tchernia, 1980).

The water fluxes of the thermohaline circulation pose somewhat more of a problem. Although the general flow patterns of water masses in CYCLOPS (Keir, 1988) and PANDORA (Broecker and Peng, 1986) are similar, significant differences exist in the extent of ventilation. An important difference is the amount of Antarctic deep water formation, which differs by about 50%. Also the Hamburg Global Circulation Model (GCM) (Maier-Reimer and Hasselman, 1987) is in some respects different from both former models. We studied the results of several circulation patterns, one intermediate to those of CYCLOPS and PANDORA, and two others as closely similar to CYCLOPS and PANDORA as possible, yet reconstructed to fit within limits of the MENU configuration. Although the results differ in detail, general trends are largely similar. Due to the larger vertical resolution of MENU, depth levels of inflow and outflow of water masses can be separated, enabling one to study the direct effects of water masses on the distributions of Cd and PO<sub>4</sub>. The exception is the Antarctic where upwelling and downwelling are combined into one box, as is the case also in CYCLOPS and PANDORA. Due to a fairly limited amount of Cd data for this region (Bordin et al., 1987; Martin et al., 1990; Nolting et al., 1991; Westerlund and Öhman, 1991), a more sophisticated configuration of this area cannot be constrained.

In addition to advective fluxes, vertical eddy diffusion was introduced. It was found that within observational limits (Sarmiento et al., 1976), the vertical distribution of the value of the vertical eddy diffusion coefficient,  $k$ , significantly influ-

enced the position of the dissolved nutrient maxima. The final values of  $k$  used in the model, which were within limits inferred from the oceanic

distributions of radiotracers (Sarmiento et al., 1976), were obtained by tuning  $k$  so as to yield the most realistic distribution of  $\text{PO}_4$  (Table 3).

TABLE 3

Initial conditions of MENU simulations

<b>Interglacial ocean</b>		
<i>Physical parameters</i>		
1 eddy diffusion coeff.	0–1000 m depth	2000 $\text{m}^2/\text{yr}$
	1000–3700 m depth	4000 $\text{m}^2/\text{yr}$
2 advective flux	three configurations:	
	MENU	$\text{Sv} = 10^6 \text{ m}^3/\text{s}$
	PANDORA (Broecker and Peng, 1986)	
	CYCLOPS (Keir, 1988)	
3 depth ocean		3750 m
4a area ocean	Arctic	0.011 $10^6 \text{ km}^2$
	Atlantic	0.105
	Antarctic	0.040
	Indo-Pacific	0.206
4b Tchernia ocean (Tchernia, 1980)	Arctic	0.014
	Atlantic	0.074
	Antarctic	0.077
	Indo-Pacific	0.196
<i>Biological parameters</i>		
1 primary production-efficiency factor	Arctic	0.2
	Atlantic	1.0
	Antarctic	0.1
	Indo-Pacific	1.0
2 export production factor		$0.2 \pm 0.05$
3 remineralization	function Cd, $\text{PO}_4$ :	$[(\text{exp. prod. at } 100 \text{ m}) \times \{160/\text{depth}\}^x]$ ,
with $x < 1.0$ , Cd has deeper remineralization function than $\text{PO}_4$ ,		
a remineralization factor Cd		1.0; 0.9; 0.75; 0.6
4 Cd/ $\text{PO}_4$ ratio incorporation during PP, fractionation factor $f$ :		
a one $f$ all oceans	Redfield ocean	0.295 $\text{nmol}/\mu\text{mol}$
	pref. Cd-uptake	0.42; 0.48
b regionally variably $f$ , two different scenarios (different plankton communities)		
	Arctic	0.17
	Atlantic	0.42
	Antarctic	0.52
	Indo-Pacific	0.42
		0.4
<b>Glacial ocean</b>		
<i>Physical parameters</i>		
1 advective fluxes	Glacial configuration MENU:	
		1. NADW 50% of interglacial
		2. NADW injected at 1000–2000 m depth
		3. increased low latitude subsurface mixing (upwelling)
<i>Biological parameters</i>		
1 primary product. efficiency factor		
low Antarctic productivity	Antarctic	0.1
high Antarctic productivity	0.5	
3 remineralization factor Cd		0.6

TABLE 3 (continued)

<i>Biological parameters</i>				
4	Cd/PO <sub>4</sub> ratio incorporation during PP, fractionation factor <i>f</i> :			
b	regionally variably <i>f</i>	normal (= low) Ant productivity		high productivity
		Arctic	0.17	0.085
		Atlantic	0.42	0.35
		Antarctic	0.52	1.7
		Indo-Pacific	0.42	0.4
c	different plankton community, stimulated productivity diatoms due to increase atmospheric dust:			
		Arctic	0.17	
		Atlantic	0.48	
		Antarctic	0.17	
		Indo-Pacific	0.48	

### *Productivity and remineralization of organic material*

The model is assumed to be closed internally, that is, there is no net sedimentation and no input into the oceans of Cd and PO<sub>4</sub>. This is a reasonable assumption, in view of the large residence times of both elements ( $\tau_{\text{Cd}} \approx 18,000$ –180,000 yr depending on the selected rate term; Boyle et al., 1976; Bruland, 1980; Balistrieri et al., 1981; Martin et al., 1989;  $\tau_{\text{PO}_4} \approx 100,000$ –200,000 yr; Broecker and Peng, 1982). No attempt was made to model primary productivity (PP) mechanistically. PP was coupled directly to surface water PO<sub>4</sub> concentrations. PO<sub>4</sub> is converted into PP using a conversion factor, tuned so as to yield reasonable yearly productivity numbers (from Berger, 1989). In the polar seas productivity is not as efficient in stripping nutrients from surface waters as in the temperate ocean, and therefore a productivity factor was introduced to simulate the integrated effect of various factors limiting PP in these waters. For the Interglacial, this factor was tuned to yield reasonable yearly productivity numbers as well as preformed PO<sub>4</sub> concentrations (Broecker et al., 1985). We realize that the global primary productivity estimate obtained in this way underestimates the real value due to exclusion of coastal and shelf waters and upwelling areas. The influence of these areas on the biogeochemical cycling of nutrients and trace metals in open ocean waters is not well understood. Whatever their contribution may be, the role of the biological pump will be underestimated by our model (as in most box models;

Broecker and Peng, 1986; Keir, 1988; Volk and Liu, 1988).

Remineralization of organic matter was attributed solely to sinking particulate organic matter (POM). In previous models, the importance of slowly degrading Dissolved Organic Matter (DOC) has been emphasized and shown to yield realistic tracer distributions (Sarmiento et al., 1988a; Sarmiento et al., 1989). We have decided not to include DOC in our model for various reasons, the most important being that its role in trace metal cycling is unknown. Also, using only sinking POM, MENU yields distributions of Cd and PO<sub>4</sub> sufficiently similar to their real distributions, that inclusion of DOC was deemed an unnecessary complication of the model, yielding little additional information. The remineralization function was adapted after the sediment trap data by Martin et al. (1987) (Table 3). POM reaching the lowest box is completely remineralized there, thus simulating complete oxidation of organic matter on the seafloor with no net burial. Export production (*f*) was allowed to vary with PP as indicated by field measurements (Betzer et al., 1984; Berger et al., 1989), but was usually on the order of 0.2. Large *f*-values resulted in excessive loss of nutrients from surface waters, leading to decreased PP and deep dissolved maxima of PO<sub>4</sub> and Cd.

### **The Interglacial ocean**

The initial values of the model parameters, tuned to reproduce the oceanic distribution of PO<sub>4</sub> as closely as possible, are listed in Table 3.

Figure 7 compares the model derived distribution with the real distribution (Bainbridge, 1980; Craig et al., 1982). In general the similarity is good. For the Atlantic Ocean, the boundaries between AAIW, NADW and AABW are somewhat more diffuse than in the real ocean. This could be due to too high values for exchange between these water masses, but also due to taking an average for the entire Atlantic Ocean. Thereby the north-south and east-west asymmetry, which is so characteristic of the modern Atlantic, is neglected.

The distribution of Cd was simulated, paying special attention to reproducing the following features:

(1) surface waters with low Cd/PO<sub>4</sub> ratios, except in the Antarctic Ocean;

(2) rapidly increasing Cd/PO<sub>4</sub> ratios in the thermocline and more or less constant values at or above the dissolved maxima of Cd and PO<sub>4</sub>;

(3) deep water Cd/PO<sub>4</sub>-ratios increasing from the Atlantic to the Pacific;

(4) a change in slope in the Cd-PO<sub>4</sub> relationship between the Atlantic and the other oceans.

These conditions were tested with three scenarios:

(1) Fractionated uptake of Cd during primary productivity, resulting in sinking POM enriched in Cd. The fractionation is allowed to vary regionally, in response to differences in the phyto- and zooplankton community. Note that in absence of an ecological model for the surface ocean, this is similar to stating preferential excretion of PO<sub>4</sub> by grazers, resulting in sinking POM depleted in PO<sub>4</sub>. What is important is that Cd and PO<sub>4</sub> have similar remineralization functions.

(2) Fractionated remineralization of Cd and PO<sub>4</sub> from sinking POM such as proposed earlier (Boyle, 1988a). Cd is slightly more refractory than PO<sub>4</sub>. Cd and PO<sub>4</sub> are not fractionated during PP.

The various model parameters of each scenario are listed in Table 3.

## Results

### Scenario 1

The results of scenario 1 are depicted in Fig. 8. If we assume a Redfield-type ocean, the oceanic Cd/PO<sub>4</sub> ratio is kept on the ratio of their respective inventories as in the case of PO<sub>4</sub> and NO<sub>3</sub> (Fanning, 1992). One ratio is observed everywhere in the oceans. In case of preferential incor-

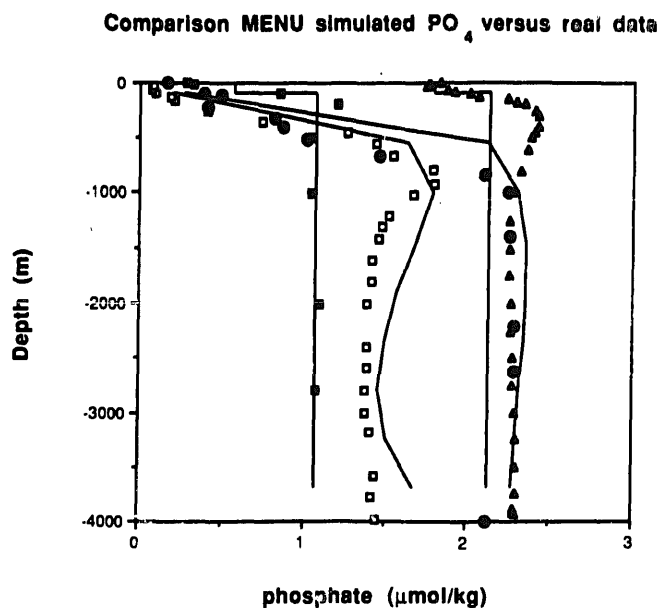
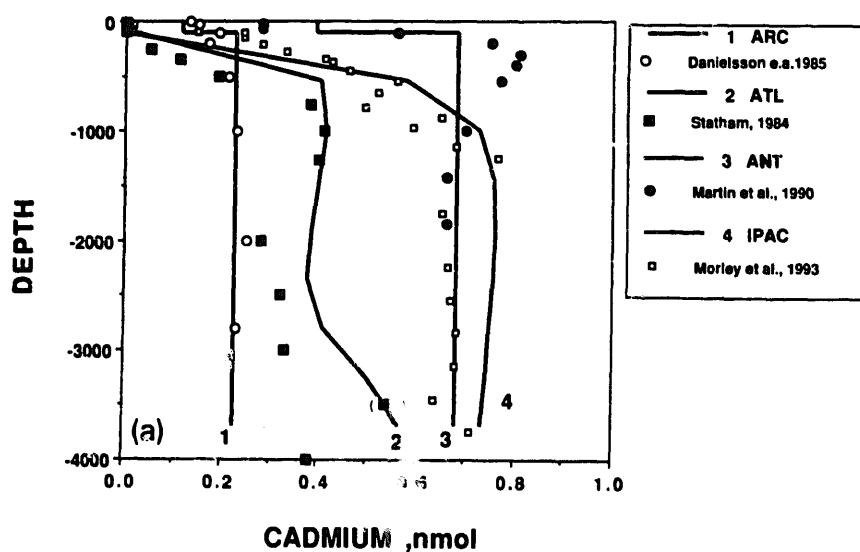
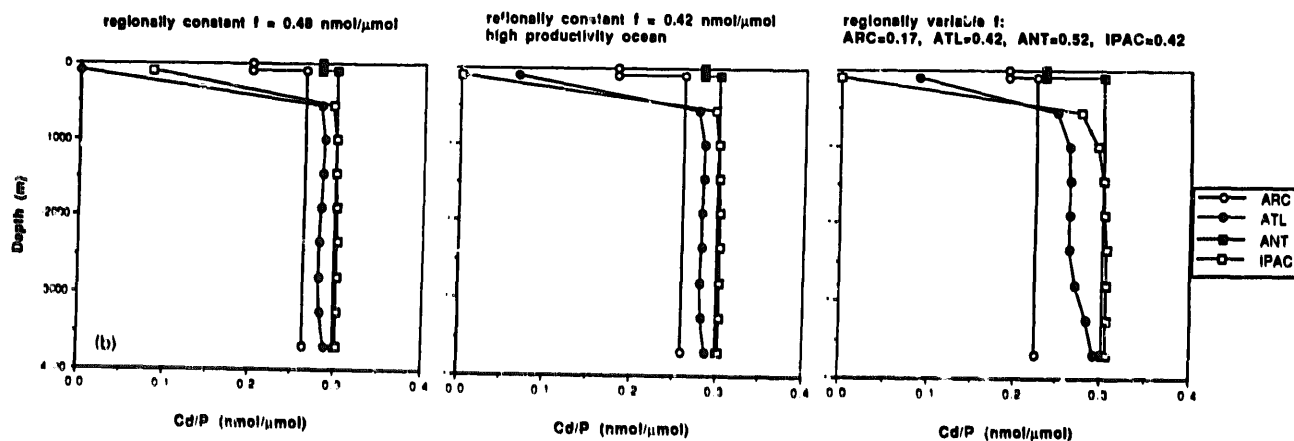


Fig. 7. Comparison of MENU simulated PO<sub>4</sub> profiles with GEOSecs PO<sub>4</sub> profiles. Solid drawn lines are MENU simulated profiles, with ocean boxes indicated in graph. GEOSecs data are from GEOSecs 6, black squares, north Atlantic Ocean; GEOSecs 36, white squares, west equatorial Atlantic Ocean; GEOSecs 78, white triangles, Southern Ocean; GEOSecs 424, black circles, west equatorial Indian Ocean.

## MENU simulated Cd profiles in comparison with measured profiles



## FRACTIONATION DURING UPTAKE



## Fractionation during uptake

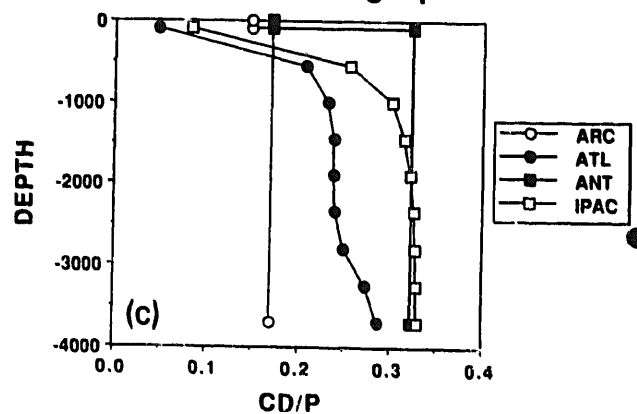


Fig. 7. Continued.

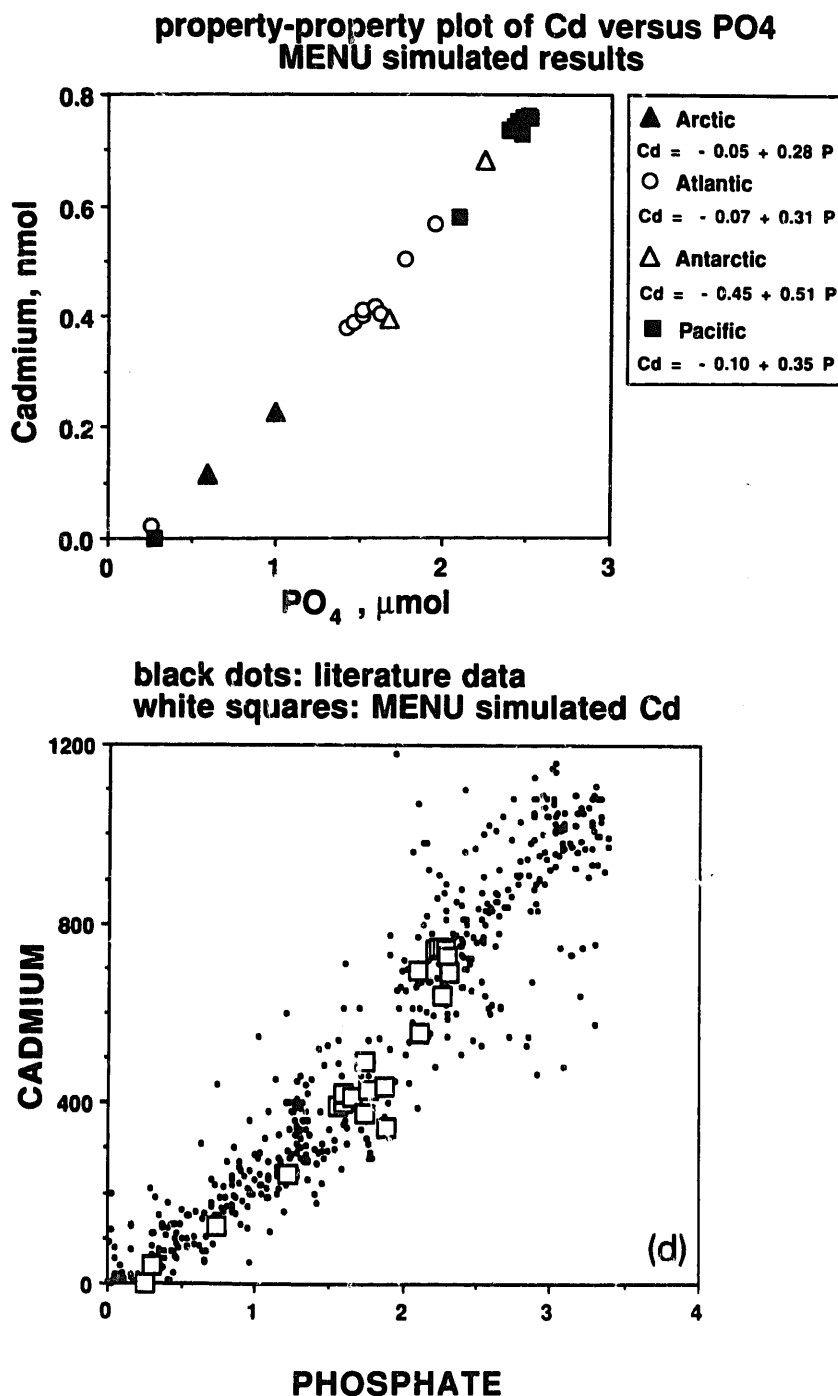


Fig. 8. MENU simulated results for Interglacial Ocean for Cd and Cd/PO<sub>4</sub> ratios, Scenario 1, fractionation of Cd and PO<sub>4</sub> during uptake. (a) Comparison of MENU Cd profiles with literature data. (b) Vertical profiles of Cd/PO<sub>4</sub> for various uptake scenarios for "normal" oceanic boundaries (Antarctic bounded by  $\approx 52^\circ\text{S}$ ). Cd/P ratios organic matter correspond to parameter conditions in Table 3: regionally constant values, 0.42 and 0.48 nmol/kg, the former was used in combination with increased subsurface ventilation (upwelling) leading to higher annual primary productivity numbers. Regionally variable fractionation factors: Arctic 0.17, Atlantic 0.42, Antarctic 0.52, Indo-Pacific 0.42 nmol/ $\mu\text{mol}$ . (c) Same for "Tchernia ocean" (Tchernia, 1980), with Antarctic Ocean bounded by  $40^\circ\text{S}$  latitude. Cd/P ratios organic matter from Table 3; Arctic 0.17, Atlantic 0.42, Antarctic 0.52, Indo-Pacific 0.42 nmol/ $\mu\text{mol}$ . (d) Property-Property plots of Cd versus PO<sub>4</sub>, upper panel for MENU simulated results only. Fractionation factor during uptake: Arctic 0.17, Atlantic 0.42, Antarctic 0.52, Indo-Pacific 0.42 nmol/ $\mu\text{mol}$ . Lower panel, MENU results in comparison with global Cd/PO<sub>4</sub> plot (from De Baar et al., submitted). Fractionation factors during uptake Arctic 0.085, Atlantic 0.35, Antarctic 1.7, Indo-Pacific 0.4 nmol/ $\mu\text{mol}$ .

poration of Cd during primary production, with one fractionation factor for all oceanic regions, surface water Cd/PO<sub>4</sub> ratios decrease to low values. Lowest values are observed in the low-latitude oceans and relatively high values in Antarctic surface waters, not dissimilar to the real situation. The Cd/PO<sub>4</sub> ratios show a rapid increase with depth in the upper thermocline. In the Indo-Pacific Ocean they reach constant values at or just above the individual dissolved maxima of Cd and PO<sub>4</sub>. Deep water ratios in the Atlantic Ocean show the strong influence of AABW, leading to high ratios in deepest waters. Also, deep water ratios gradually increase from the Arctic to the Indo-Pacific Ocean. Actual Cd concentrations are in good agreement with measured values (Fig. 8a). Realistic Cd/PO<sub>4</sub> ratios are obtained with fractionation factors larger than 480 pmol/μmol. This is within the range of ratios measured for surface suspended particulate matter (Collier and Edmond, 1984; Abe and Matsunaga, 1988; Sherrell, 1989). A larger separation between the Atlantic and Indo-Pacific Ocean is also obtained with a different choice for the oceanic boundaries. If the Antarctic is defined according to Tchernia (1980) (south of the 40°S parallel), the surface of the Atlantic Ocean decreases in favour of that of the Antarctic. Keeping the plumbing constant, the residence time of deep Atlantic water decreases, leading to lower Cd and PO<sub>4</sub> concentrations, and due to the reduced contribution of the biological pump for that region, results in lower Cd/PO<sub>4</sub> ratios. We do not suggest that this is a more realistic representation of oceanic circulation and the results are of course model determined. However, it does show that within the limits of the oceanic configuration there is some variability in biogeochemical distribution of metals and nutrients, resulting only from differences in ocean volumes, configuration and residence times. Obviously, since the model is closed with respect to in- and output of Cd and PO<sub>4</sub>, and the Cd/PO<sub>4</sub> ratio of sinking organic matter is fixed at one value, a property-property plot of Cd versus PO<sub>4</sub> does not exhibit the typical "kink".

However, the fractionation constant need not be constant regionally at all. Cd/PO<sub>4</sub> ratios of

surface suspended particulate matter do show regional variability. High dissolved Cd/PO<sub>4</sub> ratios in North Atlantic surface waters (see references in De Baar et al., submitted) suggest that in Arctic waters preferential incorporation of Cd may be relatively unimportant. In the model we have chosen a low fractionation factor for the Arctic Ocean. It has been suggested that low preformed Cd/PO<sub>4</sub> ratios in AAIW may be the cause of the kink in the Cd-PO<sub>4</sub> plot (Doroshevich and Boyle, 1992; Frew and Hunter, 1992). AAIW would ventilate the ocean with a preformed signal with low Cd/PO<sub>4</sub> ratios. Although the observational evidence for this theory is at least equivocal (see previous discussion), we have introduced this in our model by giving the Antarctic a high fractionation factor. When allowing for this regionally varying fractionation between Cd and PO<sub>4</sub>, two interesting features are observed. First, the plot of Cd versus PO<sub>4</sub> now indeed shows a kink. Lowest slopes are obtained for Arctic waters, although a negative Cd intercept is found, in contrast with measured data, depicted in Fig. 4, which have a positive Cd intercept. Highest slopes are found for the Antarctic in good agreement with measured data. Secondly, due to the lateral advection of waters from the Antarctic with high Cd/PO<sub>4</sub>-ratios, Cd/PO<sub>4</sub> ratios in deep Indo-Pacific waters continue to increase below the dissolved maxima of Cd and PO<sub>4</sub>. The downward increase is not large, but the trend is significant and probably limits the degree of freedom in regionally varying the fractionation factor. Unrealistic results are obtained if the fractionation factor in Arctic surface waters is very high or that in Antarctic surface waters is low. As can be seen from Fig. 8b, it is possible to play with the magnitude of the fractionation factor but that does not significantly change the major features described above.

### Scenario 2

In scenario 2 the fractionation factor during primary production is set at the "Redfield" ratio, but Cd is given a slightly deeper remineralization function than PO<sub>4</sub> (Fig. 9). This scenario yields generally similar results as scenario 1. Cd/PO<sub>4</sub> ratios of surface waters are low, with highest

## Fractionation during remineralization

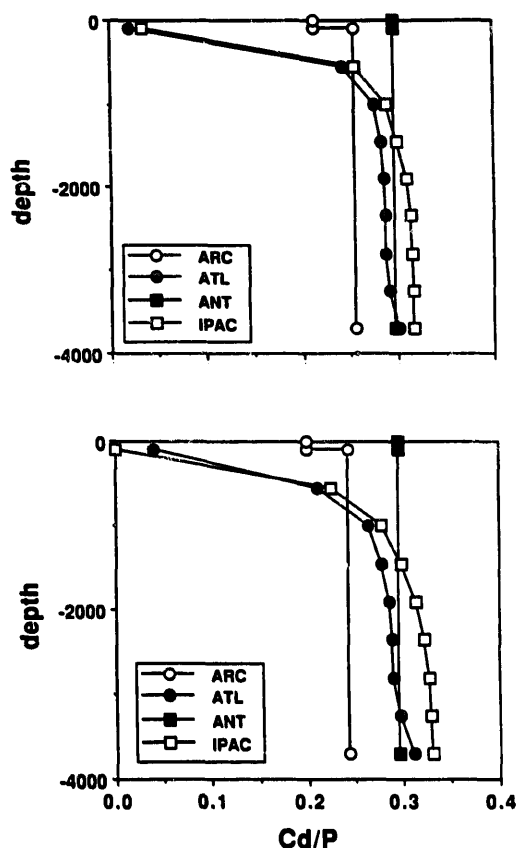


Fig. 9. MENU simulated results for Interglacial Ocean for Cd and  $\text{Cd}/\text{PO}_4$  ratios. Scenario 2, fractionation of Cd and  $\text{PO}_4$  during remineralization. Upper panel for remineralization function Cd with  $x = 0.75$ , lower panel,  $x = 0.6$ , see Table 3.

values for the Antarctic. Also, the ratio increases rapidly with depth. The ratio increases from the deep Arctic Ocean to the deep Indo-Pacific Ocean. Also, Indo-Pacific waters have a steeper slope than Atlantic waters, thus giving rise to the kink in the  $\text{Cd}-\text{PO}_4$  plot. The slope for Antarctic waters is however lowest of all oceanic regions, in contrast with the results of scenario 1 and the real ocean. As expected, scenario 2 further results in  $\text{Cd}/\text{PO}_4$  ratios increasing with depth, hence a decoupling of the dissolved maxima of Cd and  $\text{PO}_4$ . In addition, the  $\text{Cd}/\text{PO}_4$  ratio of deep Atlantic water becomes larger than the value for the Antarctic. If the fractionation factor of the remineralization function is kept low ( $x = 0.9$ , Table 3), the vertical redistribution of Cd and  $\text{PO}_4$  and the downward increase of the ratio come within the uncertainty of measured data

(not shown). However, in that case, the difference between the deep water  $\text{Cd}/\text{PO}_4$  ratios of the Atlantic and Indo-Pacific Oceans is greatly reduced.

The most realistic model simulations are obtained if Cd and  $\text{PO}_4$  are fractionated, either during primary production and/or during remineralization. The latter process also yields some features which clearly do not correspond with the field data, but we realize that the model is too simple to conclude that this scenario would not be realistic. Since regionally varying fractionation during primary production yields quite realistic model results, it appears that the composition of the plankton community may have been an important parameter in determining the oceanic  $\text{Cd}-\text{PO}_4$  relationship through geological time. We shall now look at the influence a change in oceanic conditions, such as may have occurred during a Glacial period, has on the  $\text{Cd}-\text{PO}_4$  relationship.

## The Glacial ocean

From the sedimentary record we know that the oceanic conditions may have greatly differed between Interglacial and Glacial times (Broecker, 1992). A quantitative interpretation of this information still contains considerable uncertainties, but for many changes a good estimate of minimum and maximum values can be obtained. We do not intend to give an extensive study of all possible Glacial scenarios. The aim of this Glacial ocean run is to see if the modern  $\text{Cd}-\text{PO}_4$  relationship changes in response to changing oceanic conditions. From the many Glacial scenarios which can be envisioned, the results of one, with the following assumptions, are discussed:

(1) reduction, but no cessation of the formation of NADW by 50% (Keir, 1988; Broecker and Denton, 1989);

(2) similar total ventilation rates as for the modern ocean (Andr e et al., 1986);

(3) increased low latitude subsurface upwelling due to increased mean wind stress field;

(4) increased Antarctic productivity;

(5) changes in the  $\text{Cd}/\text{PO}_4$  ratio of remineralizing organic material in response to a hypothesized change in phytoplankton community;



(6) relative changes in the oceanic inventories of Cd and  $\text{PO}_4$ : as an example the Glacial scenario was also run with an oceanic Cd inventory increased with 15% relative to the  $\text{PO}_4$  inventory. For this scenario evidence is lacking).

### Results

If only the oceanic circulation is changed, the oceanic distribution of the Cd/ $\text{PO}_4$  ratio converges to an intermediate value, being the average value of the modern ocean (Fig. 10). The asymmetry between the four ocean regions is greatly reduced though not completely abolished. The profiles of Cd and  $\text{PO}_4$  show dissolved maxima which lie much deeper than in today's ocean (Fig. 11). For the Atlantic Ocean, this results in lower concentrations in intermediate waters and higher concentrations in deep waters, in good agreement with Cd/Ca data (Boyle and Keigwin, 1987; Bertram, pers. comm., 1993). This effect is enhanced if the Antarctic productivity is increased (not shown), as was simulated earlier with the CYCLOPS model (Keir, 1988; Keir, 1991). In absence of regionally varying fractionation of Cd and  $\text{PO}_4$  during uptake, the Cd- $\text{PO}_4$  relationship does not change between Glacial and Interglacial times, since the slope is determined by one, constant fractionation factor. What changes is the oceanic distribution of the Cd/ $\text{PO}_4$ -ratio in deep water, but the functional relationship remains the same. However, if the fractionation factor is allowed to vary regionally, the different circulation by itself already results in a changing Cd- $\text{PO}_4$  relationship, since the relative contributions of the various plankton communities is changed with a different circulation (Fig. 12a). Obviously, the same result is obtained if the fractionation factor is changed in response to a different composition of the plankton communities.

A similar result is obtained in case of fractionated remineralization (Fig. 12b). For example, during a Glacial, the Cd/ $\text{PO}_4$ -slope for the Indo-Pacific Ocean is significantly different from that during an Interglacial ocean. Lastly, the average Cd/ $\text{PO}_4$  ratio of deep waters is directly proportional to relative changes in the invento-

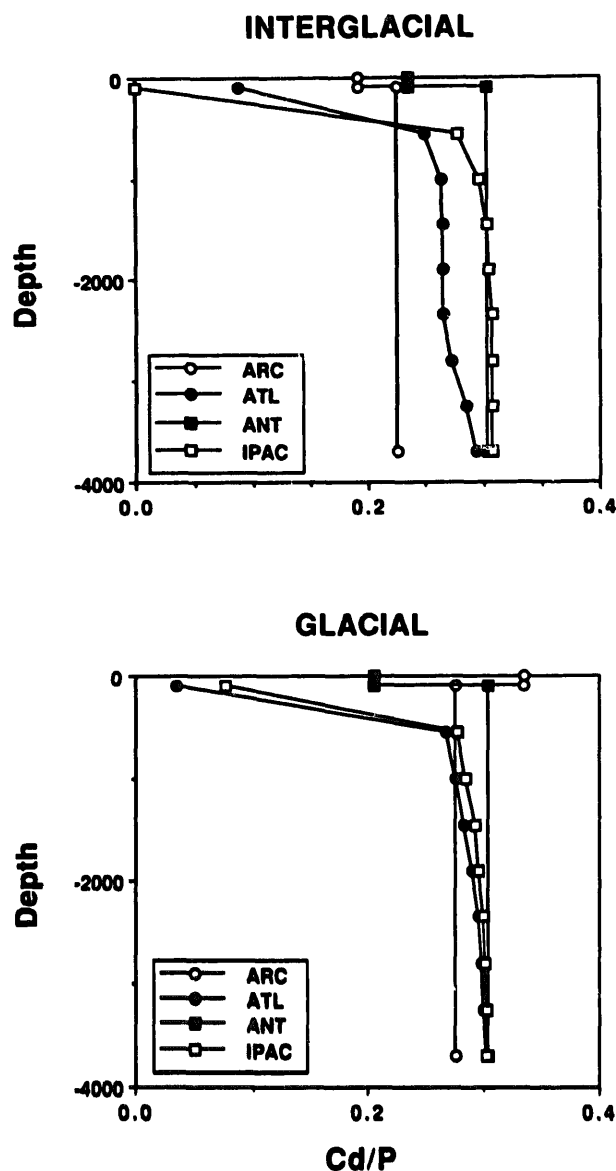


Fig. 10. MENU simulated results for Glacial Ocean. Vertical profiles of Cd/ $\text{PO}_4$  ratio for Glacial (lower panel) in comparison with Interglacial (upper panel). Both runs are for fractionation during uptake, factors are (Table 3): Arctic 0.17, Atlantic 0.42, Antarctic 0.52, Indo-Pacific 0.42 nmol/ $\mu\text{mol}$ .

ries of Cd and  $\text{PO}_4$ . Thus, if the various Glacial scenarios have any realistic value, there is little reason to assume that the oceanic Cd/ $\text{PO}_4$  relationship remains constant through geological time.

### Statistical considerations to estimating Cd, $\text{PO}_4$ or D from linear relationships

In the previous sections, various linear relationships between variables have been discussed

which have been used to estimate one property as a function of the other (e.g. estimating  $D$  from the relationship between  $Cd/Ca$  in box core tops with ambient  $PO_4$  and subsequently estimating  $Cd$  from the  $Cd-PO_4$  relationship). Although the fitting of linear relationships to data is one of the most frequent statistical activities, there is still considerable debate on how best to do it. Theoretically robust statistical techniques are available, but unfortunately, in the real world these one-would-wish-it-were-so statistics seldom apply. In using linear relationships not for explanatory but for predictive purposes, the most commonly used method is still taking the coefficients of ordinary least square regression (OLS), performed on a bivariate population. This method however often yields erroneous results, since the conditions underlying OLS hardly ever apply and since confidence intervals are seldom taken into account. The latter may greatly reduce the precision with which parameters can be estimated, possibly to the extent that the scatter about the data rivals the range in the observations.

In straight line analysis, usually four models representing the relationship between two variables are distinguished (Acton, 1959; Sprent and Dolby, 1980), which reflect the variance of the variables. Each model has its own description of the relationship between the two variables and in

case the model does not apply, the description lacks mathematical and statistical support. In other words, if OLS does not apply, the coefficients of linear regression calculated by statistical programs using OLS are not meaningful. The way in which data are usually represented in property-property plots, is by showing the means of the variables measured on random samples, with omission of all sources of error. This optimistic approach would correspond with model *I*, shown in Fig. 13a. In this model the data are samples of a bivariate, normally distributed population, in this case of  $Cd$  and  $PO_4$ . Although attractive, this assumption is clearly not valid as both  $Cd$  and  $PO_4$  are at least subject to analytical errors, which are not negligible. In addition,  $Cd$  and  $PO_4$  may not be completely mechanistically correlated (in fact there is little reason to assume they are), in case of which another source of error is introduced about which we know nothing.

Model II corresponds to classical OLS (Fig. 13b). In this model, the  $X$ -value (in our case  $PO_4$ ) is assumed to be known exactly and all the variance is attributed to the  $Y$ -value ( $Cd$ ). When examining individual profiles of  $Cd$  and  $PO_4$  one is inclined to believe this would be a good approximation to reality.  $PO_4$  concentrations usually show much higher precision than  $Cd$  data. However, at close inspection it appears that the preci-

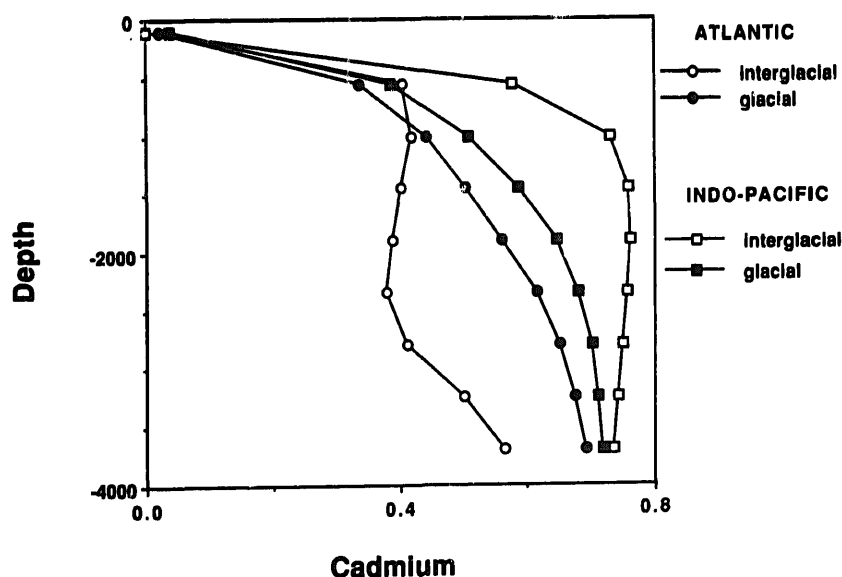


Fig. 11. MENU simulated  $Cd$  profiles, in  $nmol/kg$ , for Interglacial versus Glacial Ocean.

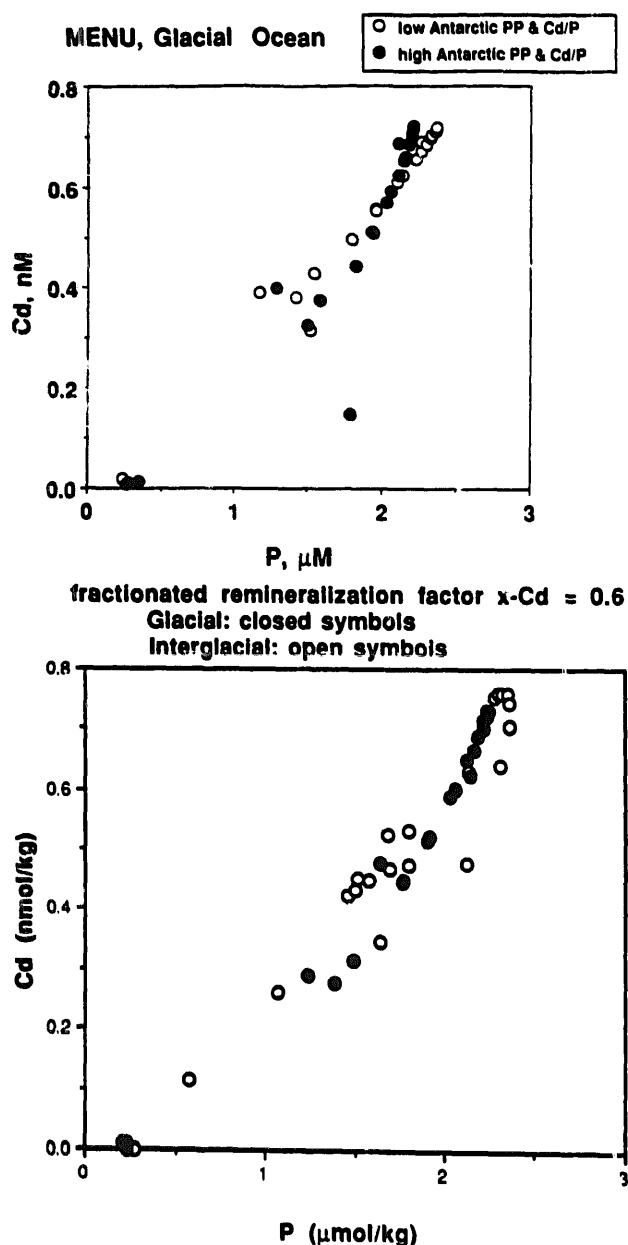


Fig. 12. Property-property plots of Cd versus  $\text{PO}_4$  for Glacial Ocean. Upper panel shows effect of Glacial circulation on Cd/ $\text{PO}_4$  relationship with fractionation during uptake. High Antarctic productivity factor = 0.5 (see Table 3), fractionation factors Arctic 0.085, Atlantic 0.35, Antarctic 1.7, Indo-Pacific 0.4 nmol/ $\mu\text{mol}$ . Low (normal) Antarctic productivity factor = 0.1 (Table 3), fractionation factors Arctic 0.17, Atlantic 0.42, Antarctic 0.52, Indo-Pacific 0.42 nmol/ $\mu\text{mol}$ . Lower panel shows effect of Glacial circulation on Cd/ $\text{PO}_4$  relationship with fractionation during remineralization, for Cd, remineralization factor  $x = 0.6$  (Table 3).

sion of the  $\text{PO}_4$  data is usually excellent, but the accuracy is probably not better than 10% (see discussion in Saager et al., submitted). Many pub-

lished  $\text{PO}_4$  datasets significantly deviate from the GEOSECS/TTO-NAS datasets, which are the only global datasets which have been thoroughly intercalibrated. For Cd, we have limited ourselves to a high quality data-set (see above), showing a precision not much worse than for  $\text{PO}_4$ . The uncertainty in both variables is at least on the order of 10%, sufficiently large to reject the validity of model II.

In the common situation in which Cd and  $\text{PO}_4$  are measured on random samples from the global Cd- $\text{PO}_4$  population, model IV applies, also known as the structural relationship (Fig. 13c). We have estimates of  $X$  and  $Y$  (namely the measured mean concentrations of Cd and  $\text{PO}_4$ ), but we know virtually nothing about the variance distribution of both variables. Performing duplicate analysis on samples would yield some information on the variance distribution of the variables, but not much, since it only slightly reduces the analytical source of error and does not give information about other sources of error. The most important consequence of dealing with model IV is that the coefficients of the regression line ( $\text{Cd} = a + b(\text{PO}_4)$ ), are determined by the ratio of the individual variances  $\lambda = \sigma_Y^2 / \sigma_X^2$  (Sprent and Dolby, 1980; McArdle, 1988). In absence of information on the variance distribution, there simply is no unequivocal, mathematically rigorous solution (McArdle, 1988). From a computer simulation calculating the error magnitude of various linear regression methods, for data sets generated with different values of  $\lambda$ , it was demonstrated that for model IV the most reliable estimate of the regression line is obtained by the reduced major axis method (RMA, Fig. 13d) (McArdle, 1988). Only if  $\lambda > 3$  the coefficients may be approximated by OLS (McArdle, 1988). In the absence of information on the total variance distributions of Cd and  $\text{PO}_4$  there is no reason to assume  $\lambda > 3$ .

If the correlation coefficient is larger than 0.9, OLS and RMA virtually coincide. However, for deep waters the bivariate Cd- $\text{PO}_4$  distribution is significantly bimodal (De Baar et al., submitted), so that two regressions have to be used, one for  $\text{PO}_4 > 2 \mu\text{mol/kg}$ , one for  $\text{PO}_4 < 2 \mu\text{mol/kg}$  (Fig. 4). Each regression has a correlation coeffi-

cient smaller than 0.9 so that both methods (OLS and RMA) will yield different slopes and intercepts. Note that the correlation coefficients are in fact upper estimates as they were calculated with the assumption of zero variance for Cd and  $\text{PO}_4$ . The difference between OLS and RMA may be considerable (Fig. 13d). Also with RMA, in absence of information on the variance distributions, it is not possible to give accurate estimates of the correlation coefficient or confidence intervals.

Now that we know that OLS for Cd and  $\text{PO}_4$  does not enjoy rigorous statistical support, we may close our eyes and pretend that model II does apply. For deep waters (below 1000 m) the resulting regression lines are shown in Fig. 4 (from De Baar et al., submitted) with corresponding confidence intervals. At given  $\text{PO}_4$  concentration, Cd can be estimated within about 15–20% at the 95% confidence level, a larger uncertainty than proposed earlier (Boyle, 1988a). It will be

clear that more realistic estimates of Cd as a function of  $\text{PO}_4$ , taking a more rigorously statistical point of view, will be worse.

From the Cd- $\text{PO}_4$  plot for thermocline waters, it seems that the correlation is somewhat better than for deep waters (Fig. 5). A similar reasoning as above can be applied for thermocline waters. For surface waters, the correlation is poor, the correlation coefficient being on the order of 0.6. For correlation coefficients below 0.6 it is hardly worth fitting a line for predictive purposes (Sprent and Dolby, 1980). It therefore seems that application of Cd as a paleonutrient tracer for planktonic foraminifera is not very fruitful.

### The distribution coefficient

The most reliable way to assess the "distribution coefficient" between the Cd/Ca ratio of foraminifera and seawater, is by directly measuring the incorporation of Cd into foraminiferal

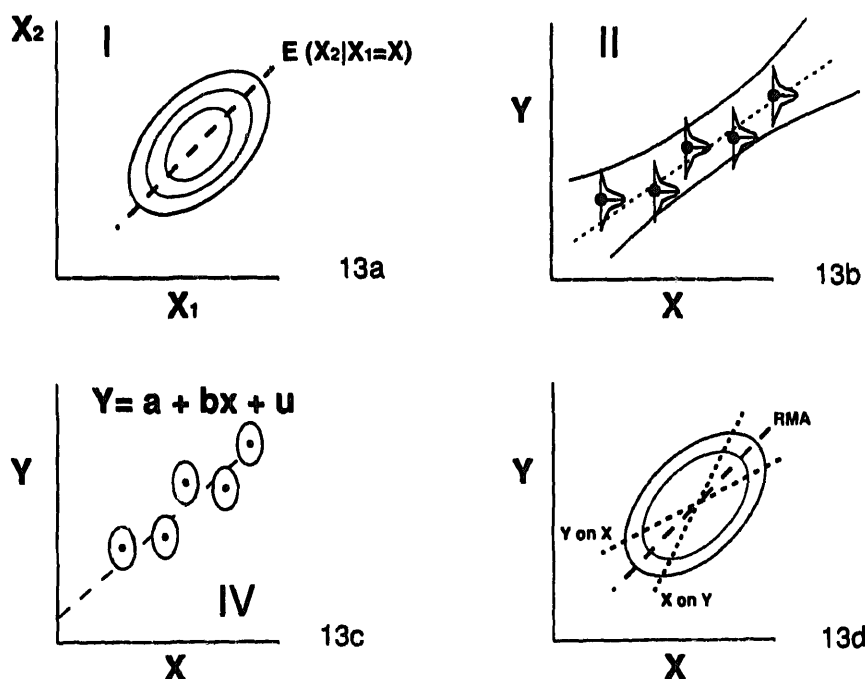


Fig. 13a. Model I: schematic distribution of a normally distributed bivariate population of  $X_1$ ,  $X_2$ . (b) Model II: schematic distribution of random samples from bivariate population,  $X$  exact, all variance is attributed to  $Y$ . Classical linear regression model, regression with ordinary least squares regression (OLS), and 95% confidence intervals for predictive purposes. Dots are means of data-pairs  $X, Y$  with variance distribution of  $Y$ . (c) Schematic distribution of random samples from bivariate population, both  $X$  and  $Y$  in error. Dots are means for data-pairs  $X, Y$ , with projection of hypothetical variance distribution. Regression of  $Y$  on  $X$  is given by  $Y = a + bX + u$ . (d) Schematic distribution of normally distributed bivariate population  $X, Y$ , both variables are in error. Shown are regression lines calculated with OLS –  $Y$  at given  $X$  and  $X$  at given  $Y$  – and calculated with Reduced Major Axis method. Note the difference in slopes of the regression lines.

shells using a radioactive Cd-tracer. Thermodynamically speaking it is not a distribution coefficient, but for the sake of simplicity we shall use this term. Thus far, this has only been performed for planktonic foraminifera (Delaney, 1989), yielding a  $D$  of between 2 and 4, an uncertainty of 33% (Table 2). Thermodynamical distribution coefficients for inorganic precipitation of  $\text{CaCO}_3$  with Cd are about an order of magnitude higher than for biogenic carbonate. An extensive discussion of thermodynamical and kinetical factors influencing the uptake of Cd in  $\text{CaCO}_3$  has been presented elsewhere (Boyle, 1988a) and is beyond the present scope. As mentioned above, an indirect assessment of  $D$  for benthic foraminifera was obtained from comparing foraminiferal Cd/Ca ratios from box core tops with the ambient seawater  $\text{PO}_4$  concentration (Boyle, 1988a). The problem with this estimate is similar to that of the dissolved Cd/ $\text{PO}_4$  relationship, namely that, despite the encouraging correlation, the relationship is not ideal due to the large non-zero intercept. Hence, analogous to the Cd/ $\text{PO}_4$  relationship, it is likely to change throughout geological time as well. Ignoring this fact, a  $D$  for the modern ocean can be estimated by relying on the relationship between Cd and  $\text{PO}_4$  given in Table 1. This yields a distribution coefficient very similar to the directly obtained estimate (Table 2). In this estimate statistical considerations, such as discussed above, were not included. This would add considerably to the variance already present when directly comparing Cd/Ca with ambient  $\text{PO}_4$  (Boyle, 1988a). As a result,  $D$  will exhibit a much larger range than suggested in Table 2, thus coming close to or more likely exceeding the range of the directly assessed  $D$ . It will be clear that an independent calibration of  $D$ , by simultaneously measuring bottom water Cd, salinity (to calculate Ca) and the foraminiferal Cd/Ca ratio is sorely needed in order to remove the circular dependance on the seawater Cd/ $\text{PO}_4$  relationship, with its variability in space and geological time.

Apart from the problems just mentioned, two other features of the distribution coefficient greatly complicate its use as a transfer function. Boyle (1992) already showed that  $D$  appeared to

be a function of depth. In addition to being a function of depth, it seems that  $D$  also shows regional variability (calculated after Boyle, 1988a; 1992), possibly related to chemical characteristics of different water masses. Since the amount of box-core top measurements is small, it is not useful to group them into small oceanic regions. Grouping of box-core tops deeper than 3000 m—below the depth dependance of  $D$ —into an Atlantic and an Antiarcto-Indo-Pacific province, yields significantly different  $D$ 's for each region. The Atlantic  $D$  is about 3.2, the other about 2.35, the difference being significant at  $\alpha = 0.05$  (95%).

The three-dimensional variability of  $D$  may have large consequences for the reconstruction of dissolved Cd for the Last Glacial Maximum (LGM) such as proposed recently (Boyle, 1992). Based on the reconstructed distribution of dissolved Cd, using one, depth-corrected value for  $D$ , it was concluded that during the LGM, Cd concentrations in the deep north and west Pacific Ocean were significantly lower than today. For the east equatorial Pacific, however, this difference was not found, nor was it observed for  $^{13}\text{C}$ . Low Cd concentrations in the NW Pacific during the LGM, would suggest that during that period the north Pacific may have experienced a deep water formation area. This north-Pacific deep water mass would have ventilated the deep Pacific with low, preformed nutrients. However, the data for the east equatorial Pacific and the  $^{13}\text{C}$  data contradict this. Such a large difference between both basins would be unexpected as the Pacific Ocean is not divided bathymetrically, as is the Atlantic Ocean. The raw Cd/Ca data thus far are inconclusive, but are not in support of a substantial difference between modern and Glacial Cd concentrations for this region. Documented box core top measurements are not yet available for the open northwest Pacific Ocean, but undocumented core tops and documented box-cores from the China Sea (presently ventilated by Pacific waters) suggest modern Cd/Ca ratios not greatly different from the LGM. In contrast, Cd/Ca ratios in core tops from the east equatorial Pacific are much higher ( $\approx 40\%$ ), both today and during the LGM. If the core top data for the northwest Pacific are reliable, this would

imply that for this area  $D$  is even lower than 2.35, namely on the order of 1.8–2.0. Preliminary data from core tops from Ontong Java plateau are in agreement with this low  $D$  (N. Ohkouchi, 1992, pers. comm.). It is not clear if Ohkouchi's cores contained 15 cm or more of Holocene sediment. To complicate matters further, the latter cores showed *higher* Cd/Ca ratios for the LGM, rather than lower, so that bioturbation could not have led to an underestimate of  $D$ . The aforementioned example shows the risks of using an improperly defined  $D$  to quantitatively interpret the Cd/Ca record.

## Discussion

In absence of a direct, independent determination of the distribution coefficient for benthic foraminifera, a quantitative interpretation of the Cd/Ca record depends on the seawater relationship between Cd and  $\text{PO}_4$ . If the Cd/Ca record is to be used as a tracer for paleonutrient distributions, it will depend on this relationship also after direct calibration of  $D$ . From the previous discussion it has become clear that, although Cd and  $\text{PO}_4$  have very similar oceanic distributions, biogeochemical fractionation between both elements results in a significant spatial variability of this relationship. The deep-water relationship is a global average of spatial variations in fractionation between both elements during primary productivity, grazing processes and remineralization of organic material. For example, large differences in Cd/ $\text{PO}_4$  ratios of organic matter have been observed between certain diatoms and other plankton species, notably for Antarctic waters (Collier and Edmond, 1984; Noriki et al., 1985). Upwelling areas often show very pronounced negative curvature of the Cd- $\text{PO}_4$  plots for upper thermocline waters (Yeats, pers. comm.; Saager et al., 1992), suggesting a rapid remineralization cycle of  $\text{PO}_4$ , leading to low surface water Cd/ $\text{PO}_4$  ratios.

The results of the model simulation suggest that a change in circulation in itself could lead to a Cd- $\text{PO}_4$  relationship different from the present ocean. The model further indicates that, if for ecological reasons the composition of the phyto-

and zooplankton communities in the surface ocean changes, this could also result in a change in the oceanic Cd- $\text{PO}_4$  relationship. One of those ecological mechanisms, discussed above, could be the increased input of Fe from atmospheric dust into surface waters during Glacial times. Culture experiments studying the effects of Fe additions on phytoplankton growth, show increased productivity and changes in species composition for surface waters with low dissolved Fe concentrations such as Antarctica and the Equatorial Pacific Ocean (Buma et al., 1991; Price et al., 1991). Other mechanisms could be due to a change in the extent of upwelling in eastern boundary upwelling systems or, for example, the monsoonal upwelling system of the Arabian Sea. Upwelling may affect phytoplankton species composition due to a change in trace metal distributions of surface waters (Bruland, 1980; Saager et al., 1992). Also, changing free metal concentrations may influence the composition of coastal relative to neritic species, since both types of plankton have different tolerance levels for trace metals (Morel and Hudson, 1984). At present, most of the theories concerning the fractionation processes influencing the Cd- $\text{PO}_4$  relationship in seawater are inevitably speculative.

Another major problem associated with the quantitative use of the Cd/Ca record is the poor definition of the distribution coefficient,  $D$ . Apart from the fact that a proper inclusion of statistical considerations presently results in a significant uncertainty of  $D$ , its depth and, possibly basin (?) dependence may prove more intrinsic factors limiting its use as a conversion factor. However, a direct calibration will no doubt remove the most acute sources of error.

## Conclusions

A quantitative interpretation of the sedimentary Cd/Ca record in terms of dissolved oceanic concentrations of Cd and  $\text{PO}_4$ , currently appears difficult, if not impossible, due to large uncertainties in the determination of the distribution coefficient and due to spatial and temporal variability of the Cd- $\text{PO}_4$  relationship. Since the raw Cd/Ca record yields results complementary to many

other established tracers ( $^{13}\text{C}$ ,  $^{18}\text{O}$ , foraminiferal abundance, etc.), a rigorous, independent calibration of  $D$  is highly desirable in order to allow the reconstruction of the oceanic distribution of Cd. Subsequently, this may turn out to be a suitable tracer of circulation and nutrient distributions. For this purpose, the mechanisms determining the relationship between Cd and  $\text{PO}_4$  need to be more closely investigated before paleonutrient distributions can be reconstructed quantitatively.

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